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بسم الله الرحمن الرحيم

شبكة المعلومـــات الجامعية

التوثيق الالكتروني والميكروفيلم

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جامعة عين شمس

التوثيق الالكتروني والميكروفيلم

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BIOPHYSICAL STUDIES OF γ-IRRADIATED GLYCOGEN/POLYVINYL ALCOHOL BLENDS DOPED WITH DYE

THESIS
SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (PH. D.) IN BIOPHYSICS

BY

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TO

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ABSTRACT

ABSTRACT

The present thesis deals with the preparation, characterization and investigation of some biophysical properties of polyvinyl alcohol (PVA), glycogen homopolymers and their blends. In addition, it shows the influence of γ-irradiation with doses in the range from 5 up to 100 kGy on the initial properties for blend sample of composition 70/30 (wt/wt %) PVA/glycogen undoped and doped with eosin. Studies were carried out using X-ray diffraction, IR spectroscopy, UV/visible spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and electrical measurements, viz., temporal variation of conduction current, I–V characteristics, dc electrical conductivity, dielectric constant, dielectric loss and ac conductivity. A correlation between the investigated properties was discussed.

Blends of PVA/glycogen of compositions 100/0, 85/15, 70/30, 50/50 and 30/70 (wt/wt %) were prepared in the form of thin films by casting technique. The dried films were optically clear, irrespective of blend composition. The glycogen homopolymer was used as a powder in the form of a pellet.

Preliminary X-ray structure analysis of homopolymers and their blend samples indicated that blending an amorphous material such as glycogen by about ≥ 50 wt % with a semi-crystalline polymer as PVA gives rise to an amorphous structure with two halo peaks at positions identical to those found in pure glycogen. X-ray diffraction patterns of all blend samples under investigation proved the miscibility of PVA and glycogen polymers in the full composition range. Irradiation of the semi-crystalline blend 70/30 (wt/wt %) PVA/glycogen with various γ-doses produced extensive chain scission of taut tie molecules plus crosslinking in amorphous regions leading to increased crystallinity and crystal perfection. A significant decrease in degree of crystallinity values is observed for pristine and irradiated blend sample doped with eosin compared to their counterparts for undoped sample.

Identification of structure and assignments of the most evident absorption bands of PVA and glycogen as well as their blends in the range 400 – 4000 cm^{-1} were studied by using Fourier transformation infrared (FTIR). The IR data indicate that there should occur a strong hydrogen bonding interaction between –OH and $-CH_2OH$ groups of glycogen and –OH groups of PVA in the blend samples. The formation of the strong carbonyl band at 1734 cm^{-1} and the appearance of the carbonyl band at 1560 cm^{-1} with γ-irradiation can be interpreted on the basis of peroxide – mediated oxidative degradation mechanism. Careful examination of the IR spectra of 70/30 (wt/wt %) PVA/glycogen doped with eosin results in the appearance of overlapping and peak shifting. This may be taken as an indication to elucidate the complex formation.

Thermal analysis employing DSC, TGA and its derivative was used to study the phase transitions and thermal stability, due to blending of the individual polymers and γ-irradiation as well as the effect of eosin additive on the blend sample of 70 wt % PVA content. Composition – dependent, single T_g was observed within full composition range in PVA/glycogen blends. To better resolve any possible overlapping T_g's, physical aging was imposed on a composition set of blend samples for the purpose of improving detectability of overlapped multiple transitions if existing. The result still showed one single T_g. The kinetic parameters such as the activation energy ($E^{\neq}$), entropy ($\Delta S^{\neq}$), enthalpy ($\Delta H^{\neq}$) and free energy ($\Delta G^{\neq}$) for all investigated samples were determined using Coats – Redfern relation.

The UV – visible spectra revealed that the blend sample of composition 70/30 (wt/wt %) PVA/glycogen has a maximum absorbance value in the wavelength range 300 – 800 nm compared to homopolymers and other blend samples. Also the value of absorbance for the undoped irradiated blend sample at 100 kGy is the highest one in the wavelength range 200 – 400 nm compared to other irradiated samples. The values of absorbance and optical parameters in UV/visible range for γ-irradiated blend sample doped with eosin showed no

significant variation with increasing γ-doses. This reflects that the addition of eosin to 70/30 (wt/wt %) PVA/glycogen makes it more resistant to γ-radiolysis than the undoped blend sample. The disappearance of the absorption band at 340 nm of PVA in blend samples provides evidence for the miscibility between homopolymers. Different optical parameters, such as absorption edge, band tail, extinction coefficient and refractive index, were calculated for the samples under investigation. It appears that there is an exponential absorption edge in the visible range $1.8 < h\upsilon < 3.3$ eV which could be attributed to the exponential distribution of localized states in the normally forbidden gap. The carrier concentration in the localized level (band tails) depends upon the total number of available sites which is different for composition ratio and γ-irradiation. The calculated color parameters such as L^*, U^*, V^*, C^*, h_{uc} and Y_e were found to be dependent on blend composition, addition of eosin and γ-irradiation.

The effect of temperature and electric field on the transient current of the samples under investigation was studied. The small values of drift mobility indicate the possibility of carrier transport by hopping mechanism. The enhanced mobility with increasing γ-dose is due to increased temporal fluctuations in the charge hopping distance which indicates that the conduction is probably due to thermally activated mobility. The study of I-V characteristics proves that the Poole-Frenkel and space charge limited conduction (SCLC) are more operative mechanisms, rather than Richardson-Schottky mechanism, at relatively high temperatures and fields. In general, the type of electric transport mechanism was affected by both temperature and γ-irradiation. The small values of thermal activation energy ≤ 0.8 eV indicated that the conduction carriers are electronic in nature while higher values of activation energy point to the participation of ionic conduction.

The dielectric properties of PVA and glycogen homopolymers and their blends as well as irradiated blend samples undoped and doped with eosin were studied by measuring dielectric constant, dielectric loss and ac conductivity as a

function of temperature and frequency. Dielectric relaxation spectroscopy separates different molecular groups of a repeating unit of a polymer with respect to the rate of its orientational dynamics. In the high temperature range (T >100°C), the σ-relaxation which is associated with the hopping motion of ions in the disordered structure of the biopolymeric materials can be measured. The electric dipole moment and the activation energy of T_g relaxation process were calculated. The correlated barrier hopping mechanism of electrons appeared to be operative. The ac parameters such as hopping distance (R, R_{min}), polaron binding energy (U_M) and coulombic barrier height (U_h) were calculated.